# 59. *The Solubility of the Copper Salts of Aromatic Carboxylic Acids in Benzene–Ethanol Mixtures.*

By Malcolm Crawford and F. H. C. Stewart.

The solubilities in benzene containing 10% of ethanol of the copper salts of a number of substituted benzoic acids have been determined. The presence of *ortho*-groups causes high solubility, *meta*-groups impart low solubility, and *para*-groups insolubility. The very few exceptions to these generalisations are considered. The effect of *ortho*-substituents is believed to be due to weakening of the crystal lattice resulting from enforced coplanarity of the carboxylate group with the aromatic ring. Such a strained lattice dissolves more readily in a solvent containing a solvating agent. The carboxylate group in the dissolved molecules will then be out of the plane of the ring. The other effects are also explained.

Certain copper carboxylates are more soluble in mixtures of ethanol and benzene than in either of the pure solvents; in the case of copper diphenylacetate this is due to the formation of an isolable complex of the salt with two molecules of ethanol (Crawford, *J.*, 1950, 2187), the complex being soluble in benzene whereas the salt is not. In the case of other copper salts, such as the phenylacetate, the complex cannot be isolated but its presence in solution is doubtless responsible for the solubility of the salt in the mixed solvents.

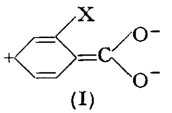
This work was extended by determining the solubility of other copper carboxylates in ethanol (1 vol.)–benzene (9 vol.) at 25°. Solubility in the fatty acid series increases rapidly from the insoluble formate (Crawford, *Nature*, 1950, **165**, 728) to the very soluble *n*-butyrate. The higher members are low-melting substances readily soluble in organic solvents. The solubility of the salts of unsaturated acids depends considerably on stereochemical configuration (Crawford, *Chem. and Ind.*, 1951, 234).

The copper salts of aromatic acids have now been examined in an attempt to explain the previous finding that the salts of many *ortho*-acids are soluble whereas the *para*-salts are insoluble in the standard solvent. It has also been noted that other physical properties vary, thus copper *o*-chlorobenzoate is bright green whereas the *para*-salt is light greenish-blue. This distinctive behaviour is of course paralleled by the known *ortho*-effects exhibited by the acids themselves. It is therefore of interest to discover whether the high solubility of the *ortho*-salts is due to the operation of an *ortho*-effect in the parent acid.

The solubilities of a number of *ortho*- and *para*-salts are presented in Table 1; values above 20 g. per 100 g. of solvent are of lower accuracy, because of experimental difficulties. The fact that a compound has high solubility is sufficient evidence for the arguments developed later. It was suggested (Crawford, *Nature, loc. cit.*), following Baddeley (*Nature*, 1939, **144**, 444), that the high solubility of *ortho*-salts, similarly to the effects shown by *ortho*-carboxylic acids generally, is due to the steric influence of the *ortho*-substituent, which would prevent the carboxyl group from lying in the plane of the benzene ring and therefore from entering into resonance with it. Consequently, forms such as (I) would be unable to contribute to the state of the molecule; hence, with the resultant decrease in ionic character, the intermolecular bonding forces in the crystal lattice would be diminished and attack by solvent and solvating molecules made easier. To establish the steric nature of the effect it is necessary to study the influence of the size of the *ortho*-substituent on solubility.

Table 1. *Solubility of copper salts in the standard solvent* (g./100 g.) *at* 25°.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| *o*-Fluorobenzoate | 3·0 | *p*-Fluorobenzoate | 0 | *o*-Bromobenzoate | 5·7 | *p*-Bromobenzoate | 0 |
| *o*-Chlorobenzoate | 2·5 | *p*-Chlorobenzoate... | 0 | *o*-Iodobenzoate ... | 6·0 | *p*-Iodobenzoate ... | 0 |
| *o*-Toluate ......... | 6·0 | *p*-Toluate ............ | 0 | Diphenyl-2-carboxylate ......... | 20 | Diphenyl-4-carboxylate ............ | 0 |
| α-Naphthoate ... | 5·9 | β-Naphthoate ...... | 0 | | | | |



(I)

A halogen atom is unsuitable as the *ortho*-substituent, since electrical influences also vary, from one halogen to another. Alkyl substituents were therefore chosen, as their size can be varied while their electrical effects can be kept at a minimum. The results of solubility determinations on the copper salts of such acids are given in Table 2. The *ortho*-salts also differ in appearance from the *para*-compounds; they vary from a bright greenish-blue (*o*-toluate) to a brilliant deep blue (*o*-*tert*.-butylbenzoate) whilst the *para*-salts are pale blue.

TABLE 2.

| | Copper salt solubility | | Copper salt solubility | M. p. of acid |
|---|---|---|---|---|
| *o*-Toluate | 6·0 | *p*-Toluate | 0 | 175° |
| *o*-Ethylbenzoate | 16·8 | *p*-Ethylbenzoate | 0·72 | 113 |
| *o*-*iso*Propylbenzoate | 23 | *p*-*iso*Propylbenzoate | 0·74 | 115 |
| *o*-*tert*.-Butylbenzoate | 35 | *p*-*tert*.-Butylbenzoate | 0 | 166 |

The solubility differences leave little doubt that the size of the substituent is an important factor. Electrical effects are likely to be slight; hyperconjugation would operate in the same direction, rendering the *tert*.-butylbenzoate less ionic and therefore more soluble, whereas the inductive effect would oppose this. Even the strong inductive effect in *o*-halogenated salts is not sufficient to suppress solubility. Hence to account for the difference between *o*- and *p*-halogenated salts steric factors must be invoked.

A logical assumption would be that the carboxyl group is rotated more and more out of the plane of the ring, but it would perhaps be better to suppose that in the crystal lattice there is a certain strain energy associated with the carboxyl group due to compulsory coplanarity with the ring. The idea of a strained crystal lattice is not unreasonable since the strain energy resulting from enforced coplanarity would only be a fraction of the lattice energy gained in packing molecules into the crystal. A compound with a strained lattice would dissolve more readily than an unstrained one in a solvent containing a solvating agent. The larger or bulkier the *ortho*-substituent, the greater will be the strain energy and hence the higher the solubility.

It would then be expected that 2 : 6-disubstituted benzoic acids would form very soluble copper salts; this is confirmed by the following figures for the solubility of copper salts in the standard solvent (g./100 g.) at 25°: 2 : 6-dimethylbenzoate, 40; 2 : 4 : 6-trimethylbenzoate, 35; 4-*tert*.-butyl-2 : 6-dimethylbenzoate, 30; and 2-methyl-1-naphthoate, 35.

Another factor which might be involved in copper salt solubility is acid strength; it is clear that the two increase in step. However, in the fatty acid series acid strength decreases while copper salt solubility increases from formic to butyric acids. Examination of other series does not reveal any significant interconnection. Acid strength and copper salt solubility are most probably being influenced similarly by the presence of the bulky *ortho*-group. Indeed it has been shown (cf. Burkin, *Quart. Reviews*, 1951, **5**, 16) that the more basic a ligand, the more stable are the metal complexes formed by it.

TABLE 3. *Acid strength and copper salt solubility.*

| Acid | $10^5K$ | Salt solubility | Acid | $10^5K$ | Salt solubility |
|---|---|---|---|---|---|
| $C_6H_5{\cdot}CO_2H$ | 6·5 | 0·1 | 2 : 4 : 6-$Me_3C_6H_2{\cdot}CO_2H$ | 37·0 * | 35 |
| *o*-$Me{\cdot}C_6H_4{\cdot}CO_2H$ | 13·5 | 6·0 | 2 : 6-$Me_2C_6H_3{\cdot}CO_2H$ | 62·0 | 40 |
| *o*-$Bu^t{\cdot}C_6H_4{\cdot}CO_2H$ | 35·1 | 35 | | | |

* The dissociation constant is given in Beilstein, **9**, 553 as $3{\cdot}75 \times 10^{-5}$ and in "International Critical Tables," Vol. VI, p. 295, as $3{\cdot}7 \times 10^{-4}$; the same unavailable references are cited. It is assumed by analogy with 2 : 6-dimethylbenzoic acid that the value given in Beilstein is a misprint.

The stability of the complexes of copper salts with alcohols is low and is probably a much less important factor in determining solubility than the lattice stability of the uncomplexed salts. The solubility apparently depends largely on the ease of disintegration of the crystal lattice by the benzene–ethanol rather than on any marked stability of the complexes formed in solution. The effect of substituents known to have a weakening influence on lattice stability was therefore examined. Since the melting point of an organic compound is mainly a measure of the ease of disintegration of the crystal lattice, it follows that any substituent which has a marked lowering effect on the melting-point should be suitable for this purpose. Ethyl, propyl, and *iso*propyl groups are known to exert such an effect, generally in much greater measure than methyl or *tert.*-butyl groups. The solubilities of the copper salts of various low-melting *m*-alkylbenzoic acids and those of the higher-melting methyl and *tert.*-butyl analogues have therefore been determined:

| *m*-Substituent | Me | Et | $\text{Pr}^n$ | $\text{Pr}^i$ | $\text{Bu}^t$ |
|---|---|---|---|---|---|
| M. p. of acid | 110° | 45° | 43° | 47° | 127° |
| Solubility of copper salt | 1·9 | 3·1 | 3·0 | 3·0 | 4·8 |

Compared with results given in Table 2 for salts of *para*-substituted acids, these results show that the presence of an ethyl group, for example, has a small, though real effect on copper-salt solubility. It would also appear from these two Tables that groups such as ethyl, propyl, and *iso*propyl, which have a profound effect in lowering the melting point of an acid, also have the power to impart slight solubility to its copper salt, which would otherwise be insoluble.

The presence, in the *meta*-position, of a substituent not having a marked lowering influence on melting point, *e.g.*, methyl or *tert.*-butyl, nevertheless causes the copper salt to be appreciably soluble. This is confirmed by the solubilities of a range of copper *meta*-substituted benzoates in the standard solvent (g./100 g.) at 25°: *m*-fluorobenzoate, 1·5; *m*-chlorobenzoate, 1·5; *m*-bromobenzoate, 1·09; *m*-iodobenzoate, 1·04; 3-bromo-4-methylbenzoate, 0·8; diphenyl-3-carboxylate, 0·87; 3 : 4-dimethylbenzoate, 1·3. These salts are seen to be appreciably soluble in benzene–ethanol, which would not be expected if solubility depended entirely on a steric *ortho*-effect.

The solubility of the copper *meta*-substituted benzoates can be taken as evidence in support of ease of lattice disintegration as a factor in copper-salt solubility. The introduction of almost any group into the *meta*-position will result in the production of a more open crystal lattice, which of course will not only be more exposed to solvent attack but will possess a lower lattice energy. This conception is supported by the considerable effect of the bulky *tert.*-butyl group in increasing solubility. Lattice widening will also occur in the *ortho*-substituted benzoates but is masked by the much greater steric effect of the *ortho*-group.

The solubility of copper salts of aromatic carboxylic acids in benzene–ethanol depends therefore upon a number of factors of varying intensity: (1) the presence of groups known to lower the melting point, a slight effect, (2) the presence of *meta*-substituents, also a small effect probably due to lattice widening in the crystal, and (3) the presence of an *ortho*-substituent, which is the major and most firmly established factor, which operates by steric action on the carboxyl group.

## EXPERIMENTAL

*Preparation of Copper Salts.*—(a) *Precipitation method.* The pure acid was neutralised (to phenolphthalein) with dilute sodium hydroxide solution. A slight excess of aqueous analytical grade copper sulphate was added with stirring, and the mixture boiled. The washed and dried copper salt was crystallised from benzene–ethanol whenever possible.

(b) *Copper carbonate method.* This method was used whenever the copper salt was soluble in water. The pure acid and an excess of copper carbonate were boiled in a large volume of water, the excess of carbonate was filtered off and the filtrate was evaporated to dryness, and the residual copper salt purified as already described.

Copper was determined by the salicylaldoxime method.

*Solubility Determinations.*—The dried copper salt was shaken in a stoppered vessel with benzene–ethanol (9 : 1, by volume) for 2—3 days at 25°. The saturated solution was quickly filtered into a tared weighing bottle, which was then stoppered and weighed. The solvent was evaporated and the residue dried to constant weight at 110°. The solubility is expressed in g. of salt per 100 g. of solvent, not as in previous papers. With values above 20 it was difficult to obtain reproducible results and such values are given to the nearest whole number.

*Copper Salts.*—The following copper salts were used [prepared by method (*a*), unless otherwise stated; solubility refers to *hot* benzene–ethanol, from which solvent the salts were crystallised unless otherwise specified].

Benzoate, a slightly soluble, blue powder (Found : Cu, 20·7. Calc. for $C_{14}H_{10}O_4Cu$ : Cu, 20·8%). o-*Toluate*, very soluble, blue needles (Found : Cu, 18·9. $C_{16}H_{14}O_4Cu$ requires Cu, 19·0%). m-*Toluate*, small bluish-green, solvated crystals (solvent lost on exposure, giving a blue powder) (Found : Cu, 18·9%). *p*-Toluate, an insoluble blue powder (Found : Cu, 19·3%) (previously prepared by Noad, *Annalen*, 1848, **63**, 294).

Diphenyl-2-carboxylate, very soluble, deep blue solvated octahedra (the bluish-green salt obtained by removal of the solvent at 100° was thermochromic) (Found : Cu, 13·7. Calc. for $C_{26}H_{18}O_4Cu$ : Cu, 13·9%) (previously prepared by Weger and Döring, *Ber.*, 1903, **36**, 881). *Diphenyl*-3-*carboxylate* (the acid was prepared by oxidation of 3-methyldiphenyl, obtained by Gomberg reaction on *m*-toluidine), soluble, blue needles (Found : Cu, 13·7%). *Diphenyl*-4-*carboxylate* (the acid was prepared as for the 3-isomer), an insoluble, pale blue powder (Found : Cu, 14·1%). α-*Naphthoate*, soluble, green needles (Found : Cu, 15·7%. $C_{22}H_{14}O_4Cu$ requires Cu, 15·7%). β-*Naphthoate*, an insoluble, pale blue powder (Found : Cu, 15·9%). 2-*Methyl*-1-*naphthoate*, bright green, solvated needles, from ethanol (solvent lost at 100°, with colour change) (Found : Cu, 14·5. $C_{24}H_{18}O_4Cu$ requires Cu, 14·6%).

*o*-Ethylbenzoate, a very soluble, bluish-green powder (Found: Cu, 17·3. Calc. for $C_{18}H_{18}O_4Cu$ : Cu, 17·6%) (Giebe, *Ber.*, 1896, **29**, 2534, prepared this compound). m-*Ethylbenzoate*, soluble bluish green needles (Found : Cu, 17·4%). *p*-Ethylbenzoate, somewhat soluble, pale blue, thermochromic needles (Found : Cu, 17·3%) (previously prepared by Fittig and König, *Annalen*, 1867, **144**, 292).

The o-iso*propylbenzoate* was very soluble in ethanol from which it separated in green plates, which lost ethanol when heated, giving a dark blue salt (Found : Cu, 16·2. $C_{20}H_{22}O_4Cu$ requires Cu, 16·3%). m-iso*Propylbenzoate*, very soluble, greenish-blue needles (Found : C, 16·1%). p-iso*Propylbenzoate*, soluble, thermochromic blue needles (Found : C, 15·9%) ; the parent acid was prepared as follows : The Grignard reagent from the mixed isomers obtained by bromination of cumene was treated with carbon dioxide, the copper salts of the resulting mixed acids were separated by extraction with benzene–ethanol, and the less soluble *para*-salt was purified through the parent acid (m. p. 115° ; from hot water). m-*Propylbenzoate*, small blue needles (Found : C, 16·1%).

o-tert.-*Butylbenzoate* was very soluble in ethanol but crystallised from methanol in dark green leaflets, which crumbled at 100° to a deep blue powder (Found : Cu, 15·3. $C_{22}H_{26}O_4Cu$ requires Cu, 15·2%). m-tert.-*Butylbenzoate* : method (a) gave the salt as a greenish-blue powder, soluble in hot benzene–ethanol; evaporation of this solution gave a duck-egg blue powder, insoluble in this solvent; the original powder became purple, then pale green when heated, and its solution in benzene–ethanol gave soluble green crystals [Found : Cu, 14·8 (duck-egg blue powder) ; Cu, 14·9% (recrystallised pale green powder)]. p-tert.-*Butylbenzoate*, an insoluble, pale blue (deepening when heated) powder (Found : C, 15·3%) ; the acid was prepared by Verley's method (*Bull. Soc. chim.*, 1898, **19**, 72).

2 : 6-*Dimethylbenzoate*, obtained as a green salt in poor yield by method (*a*) and in better yield by method (b) as a brown product, formed solvated, dark green octahedra from ethanol, or solvent-free needles (sometimes green, sometimes reddish-brown, and sometimes a mixture) from benzene–ethanol (Found : Cu, 17·4. $C_{18}H_{18}O_4Cu$ requires Cu, 17·6%) ; the parent acid, m. p. 116°, was prepared from 2 : 6-dimethylaniline through 2-bromo-*m*-xylene by Sandmeyer and Grignard reactions. 2 : 4 : 6-*Trimethylbenzoate*, preferably prepared by method (b), formed green solvated crystals from ethanol or acetone; the solvent-free salt was a green powder (Found : Cu, 16·1. $C_{22}H_{26}O_4Cu$ requires Cu, 16·3%). 4-tert.-*Butyl*-2 : 6-*dimethylbenzoate*, green solvated leaflets, from ethanol containing a little benzene; when heated these gave a dark blue powder (Found : Cu, 13·3. $C_{26}H_{34}O_4Cu$ requires Cu, 13·4%). 3-*Bromo*-4-*methylbenzoate*, a soluble blue powder (Found : Cu, 12·9. $C_{16}H_{12}O_4Br_2Cu$ requires Cu, 12·9%) ; the acid, m. p. 202°, was readily obtained by bromination of *p*-toluic acid by Derbyshire and Waters's method.

o-*Fluorobenzoate* : method (b) gave a pale blue, partially soluble, powder; the residue was Slothouwer's basic salt (*Rec. Trav. chim.*, 1914, **33**, 325) ; the solution gave the greenish-blue normal salt (Found : Cu, 18·2. $C_{14}H_8O_4F_2Cu$ requires Cu, 18·6%). *m*-Fluorobenzoate always contained some basic salt (Found : Cu, 23·0%). *p*-Fluorobenzoate also always contained some basic salt (Found : Cu, 24·1%).

o-*Chlorobenzoate*, green needles by method (b) (Found : Cu, 16·7. $C_{14}H_8O_4Cl_2Cu$ requires Cu, 17·0%). m-*Chlorobenzoate*, blue crystals (Found : Cu, 16·9%). p-*Chlorobenzoate*, an insoluble pale blue powder (Found : Cu, 17·2%), distinct from the dihydrate reported by Ephraim and Pfister (*Helv. Chem. Acta*, 1925, **8**, 379).

o-*Bromobenzoate*, preferably prepared by method (b), formed green needles (Found: Cu, 13·5. $C_{14}H_8O_4Br_2Cu$ requires Cu, 13·7%); Rhalis (*Annalen*, 1879, **198**, 107) has described a monohydrate. m-*Bromobenzoate*, green needles which lose solvent readily to give a very deep blue powder (Found: Cu, 13·8%). p-*Bromobenzoate*, an insoluble pale blue powder (Found: Cu, 13·7%).

o-*Iodobenzoate*, yellowish needles from benzene or green solvated needles from benzene–ethanol (Found: Cu, 10·5. $C_{14}H_8O_4I_2Cu,C_2H_6O$ requires Cu, 10·5. Found, in material dried at 100°: Cu, 11·4. $C_{14}H_8O_4I_2Cu$ requires Cu, 11·4%). m-*Iodobenzoate*, blue crystals which crumble to a deep blue powder when heated (Found: Cu, 11·2%). p-*Iodobenzoate*, an insoluble, pale blue powder (Found: Cu, 11·3%).

One of us (F. H. C. S.) is indebted to the Ministry of Education for Northern Ireland for a maintenance allowance.

College of Technology, Belfast.

[*Received, July 26th*, 1952.]